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Catalysts for Direct Decomposition of NO_x in Exhausts

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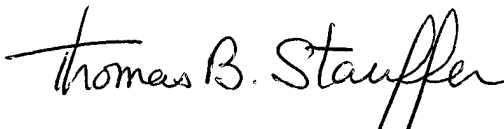
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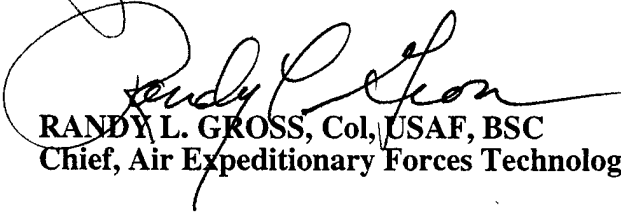
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Catalysts for Direct Decomposition of NO_x in Exhausts

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ABSTRACT

Eltron Research, Inc. is pursuing the rational development of catalysts for direct (reagentless) decomposition of NO_x. This is the most economical imaginable approach for post-combustion removal of nitrogen oxides since costs for reagent and reagent delivery (i.e., ducting, etc.) are eliminated and catalysts demonstrating activity to the present time are inexpensive (\$1 - \$4/lb). The decomposition of nitrogen oxides in simulated exhaust streams over new brownmillerite catalysts has been examined in a range of temperatures and residence times. Results are indicative of the occurrence of reagentless activity in gas streams containing up to 16 percent oxygen. Performance was nonmonotonic in temperature, with an activity maximum occurring between 550 and 600°C. For example, up to 90% conversion of NO_x at 250°C and 30,000h⁻¹ has been attained. Using CO as a reductant, at 800,000h⁻¹ and 1000°C, one catalyst removed 16 percent of 477 ppm NO in a stream also containing 16 percent O₂. These results suggest the potential efficacy of the catalysts for the direct decomposition of nitrogen oxides in high temperature (400 - 1000°C) exhaust gases, in e.g., gas turbine and diesel engines. In addition, the catalysts were found to be effective at oxidizing CO. The enhancement of activity obtained using carbon monoxide is particularly relevant in such applications.

INTRODUCTION

The direct decomposition of nitrogen oxides under lean conditions absent an added reductant, e.g., in exhaust streams of diesel engines, lean burn engines, gas turbines, and other high temperature processes, constitutes a particularly attractive approach for post-combustion removal of nitrogen oxides from these sources. Selective catalytic reduction with e.g., ammonia or urea can result in reductant slip as well as added cost from reagent storage and delivery. Optimal activity under ideally reagentless conditions is neither attainable, necessary, or desirable. Rather, utilization of oxidizable exhaust stream constituents to enhance existing reagentless activity seems to be the preferred approach under lean conditions. A direct decomposition catalyst, i.e., one which possesses activity in realistic exhaust stream fuel/air stoichiometries and utilizes only incompletely oxidized feedstream constituents without addition of these or other species is extremely desirable.

Direct decomposition catalysts have been previously reported in the literature. Tabata¹

reported on the activity of the material $\text{Ba}_2\text{YCu}_3\text{O}_{7.8}$. It was found that the material could remove approximately 18% of a stream 51 ppm in NO and 8.1% in oxygen at approximately 300°C and 15,500 h^{-1} . This catalyst demonstrated increasing activity with increasing gas stream oxygen content up to about 8 percent and a very sharp temperature dependent maximum at about 300°C. Mori, et al² reported that the materials $\text{Ba}_2\text{In}_2\text{O}_5$, $\text{Ba}_3\text{Y}_4\text{O}_9$, and BaLa_2O_4 , which possess the brownmillerite structure, demonstrated deNO_x activities which increased with a decreased temperature of order-disorder transition. In the absence of added oxygen, up to 45% of 1300 ppm NO was removed at 500°C and a space velocity of 2500 h^{-1} . Shin, et al³ evaluated the materials $\text{Ca}_2\text{Fe}_2\text{O}_5$ and $\text{Sr}_2\text{Fe}_2\text{O}_5$ for activity toward direct decomposition of NO_x . The material $\text{Ca}_2\text{Fe}_2\text{O}_5$ was inactive, but $\text{Sr}_2\text{Fe}_2\text{O}_5$ demonstrated activity for the decomposition of 3% NO in helium. Essentially 100% of NO was decomposed at 900°C but only 300 h^{-1} .

Li and Hall⁴ reported on the activity of the zeolite catalyst Cu-ZSM-5 under conditions absent reagent (e.g., hydrocarbon). Experiments were performed at high levels of NO (4%) in the absence of oxygen. At very low space velocities (1800 h^{-1}), the catalyst converted over 90% of the NO in the gas stream at 500°C. All of the reacted nitrogen oxide could not be accounted for in terms of reduction processes. Rather, appreciable levels of NO_2 were produced from the reaction of O_2 produced from NO decomposition. The addition of 10% O_2 to the reaction stream resulted in a decrease in NO conversion from 97% to 80%, pointing to some oxygen poisoning.

Another catalytic approach to decomposing nitrogen oxides is that of Lunsford, et al.⁵⁻⁷ In this case, MgO supported BaO was the catalyst. The material was found to exhibit a maximum in the decomposition of 1% NO, absent oxygen, at 630°C. The addition of 0.5% oxygen to the gas stream resulted in almost complete loss of activity at that temperature. However, most of the activity was recovered when the temperature was increased to 660°C. When only 1.2% CO_2 was added to the gas stream, the catalyst's activity decreased by almost a factor of ten.

Wu, et al,⁸ evaluated the perovskite materials LaNiO_3 , $\text{La}_{0.1}\text{Sr}_{0.9}\text{NiO}_3$, La_2NiO_4 , and LaSrNiO_4 for NO uptake, temperatures of desorption, and activity toward NO decomposition. It was found that catalyst activity increased with increasing Sr content, indicating that catalyst activity was proportional to the concentration of oxygen ion vacancies in the catalyst. The most active of these catalysts achieved its maximum activity (95% NO conversion) at 900°C. These materials were evaluated in oxygen-free streams at space velocities of 2880 h^{-1} and NO concentration of 1.5 mole% (~15,000 ppm).

More recently, the role of base promoters⁹ and oxygen ion vacancies¹⁰ in promoting direct decomposition have been studied. In the former case, it was found that the presence of sodium in Co_3O_4 promoted the direct decomposition of NO. In the latter case, the doping of perovskites with aliovalent species improved the activity of perovskites by introducing oxygen ion vacancies.

Many of these previous results were obtained under experimental conditions in which NO (>>1000 ppm) and oxygen (0%) concentrations differed greatly from those encountered in real post-combustion environments. While such conditions allow for demonstration of decomposition, they do not reflect the fact that, at most, a few hundred ppm of nitrogen oxides must compete with oxygen concentrations of up to 15 volume percent. This three order of magnitude disadvantage renders impractical any catalyst which does not make use of the Lewis acid-base properties of target molecules and catalyst.

Interaction of adsorbed nitric oxide molecules with the surfaces of such metal oxide catalysts can occur in a number of ways. The presence of oxygen ion vacancies on the catalyst surface offers unsatisfied valence and sharp electric field gradients which weaken N-O bonds,

leading to dissociation. The role of oxygen ion vacancies and their relationship to deNO_x activity has been clearly demonstrated in the literature.^{2,3,8} The adsorbed oxygen anion is then discharged via oxidation by a transition metal species in the catalyst, followed by combination into molecular oxygen and its subsequent desorption. Reoxidation of transition metal species occurs via electron transfer to adsorbed NO.

Consideration of the aforementioned requirements for reagentless deNO_x over metal oxide catalysts led us to develop new materials based on the brownmillerite structure. The stoichiometries of these materials are such as to provide a high concentration of intrinsic oxygen ion vacancies, while at the same time providing overall material stability.

EXPERIMENTAL SECTION

Catalysts described here were prepared either by the ceramic method (i.e., by grinding together constituent metal oxides and/or metal carbonates) or by decomposition of the constituent metal nitrates on a support (alumina or yttria stabilized zirconia - YSZ). Catalysts prepared by either method were calcined at 1000°C for 8 hours. Phase purity was verified by x-ray powder diffraction. X-ray diffraction powder patterns were obtained using a Rigaku Miniflex diffractometer equipped with a Cu source. Surface areas of catalysts were obtained with an ASAP 2000 surface area analyzer (Micromeritics) by measurement of uptake of nitrogen and application of the Brunauer-Emmett-Teller equation.

Temperature programmed desorption (TPD) spectra were obtained using an in-house constructed apparatus. A temperature-controlled furnace was used to heat a weighed sample of catalyst over a range of temperatures. The desorbing oxygen was measured using an in-line electrochemical oxygen sensor.

Catalyst activities were measured by passing a simulated exhaust stream over weighed catalyst powder samples heated to the desired temperature with a furnace. The gas stream contained from 475 - 1000 ppm NO in 16 percent O_2 with helium comprising the balance of the mixture. The effect of the addition of carbon monoxide, carbon dioxide, water, and sulfur dioxide to the simulated exhaust stream was also examined. NO and NO_2 were analyzed by means of electrochemical sensors specific to these respective species. Reaction products (i.e. N_2 and N_2O) were analyzed with an HP 5890-A gas chromatograph equipped with a CTR-I column (Alltech) and a pulsed thermal conductivity detector (TCD). Reactants and products were also analyzed with a Leybold-Inficon Quadrex 200 residual gas analyzer (RGA) equipped with a quadrupole mass spectrometer.

RESULTS AND DISCUSSION

An x-ray diffraction pattern for the catalyst EC-105 prepared by the ceramic method is shown in Figure 1. The diffraction pattern is dominated by one phase which has been assigned the brownmillerite structure with a unit cell size of $a = 5.90\text{\AA}$, $b = 16.3\text{\AA}$, and $c = 5.86\text{\AA}$. A small amount of a second phase was also present, but has not been identified. Nevertheless, the brownmillerite phase appears to be active, since analogs of the material not containing the second phase have comparable or greater activity.

The catalyst EC-105 displayed the TPD spectrum shown in Figure 2. The spectrum shows a common feature of brownmillerite materials: a steeply ascending portion of the curve at temperatures above 700°C, corresponding, presumably to the loss of lattice oxygen. However, an atypical feature is the peak beginning at 350°C, apparently corresponding to the desorption of relatively weakly bound surface oxygen species. The occurrence of this feature suggests that a particular catalyst can readily release surface oxygen, freeing sites for NO adsorption. It was found that the catalyst EC-105 gave an activity maximum at 400°C, almost coincident with the maximum in oxygen signal displayed in Figure 2, although there is no apparent cause-and-effect relationship between the two observations. The activity maximum almost certainly arises from a competition between the increasing dissociation rate and decreasing overall rate of NO uptake with increasing temperature.

The material EC-105 was observed to have appreciable activity under 3% O₂, 3.5% water, 15% CO₂, and 300ppm NO. However, the unsupported material was also observed to demonstrate loss of activity in the presence of water and above a certain temperature (Figure 3). For example, separate catalyst samples gave persistent activity over 140 hours at 250°C, while at 300°C, the catalyst lost activity with time. It

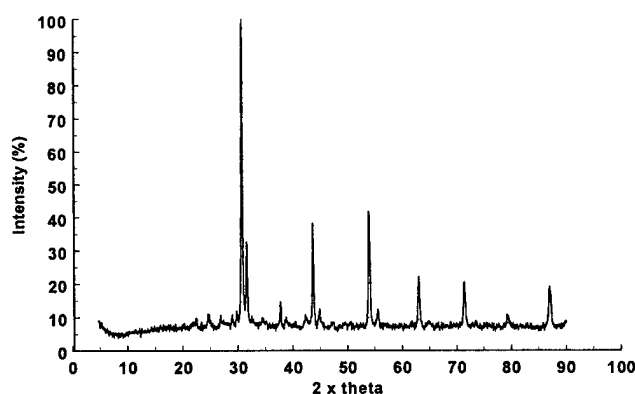


Figure 1. An x-ray diffraction pattern for catalyst EC-105.

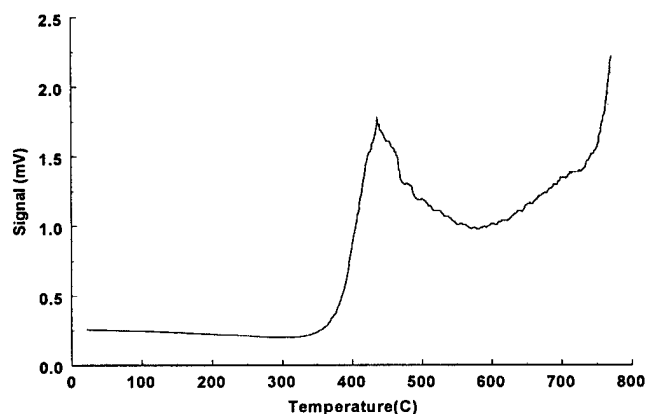


Figure 2. TPD spectrum of catalyst EC-105.

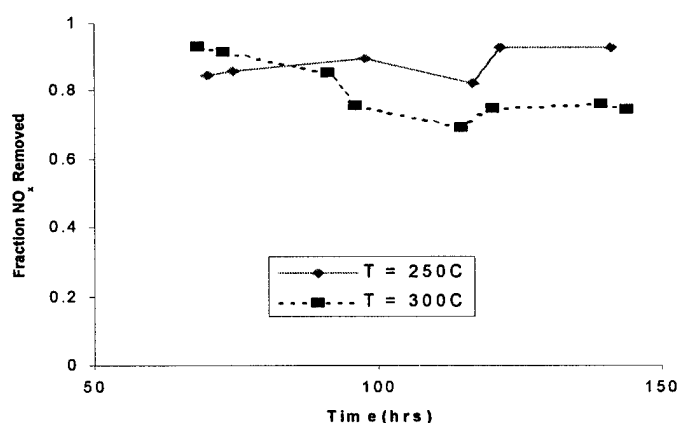


Figure 3. Plots of NO_x removal versus time obtained at two different temperatures, with each (temperature) experiment performed using separate catalyst samples.

was also observed that the catalyst formed an aggregate which tended with time to block the reactor.

A supported analog (i.e., same precursor stoichiometry in metal ions) of EC-105 was prepared by incipient wetness impregnation of neutral Brockman alumina with the appropriate metal nitrates. Initial screening of the material revealed significant activity as shown in Table 1. Data presented there were obtained under the same conditions as that for unsupported EC-105. These data shows a strong temperature dependence of catalyst activity. The primary product channel for the system was found to be to nitrogen as determined by gas chromatography measurements.

Table 1.
Data for Conversion of NO_x Over 6.3% EC-105/ Al_2O_3 (neutral Brockman).

Temperature ($^{\circ}\text{C}$)	Conversion(%)	Selectivity to N_2 (%)
250	2.8	74
300	19.8	93
350	43.8	97

This supported version of the catalyst was also found to exhibit remarkable activity for the oxidation of carbon monoxide. The data in Table 2 show that the catalyst is highly active for CO oxidation.

In spite of the material's oxidation activity, it is still able at higher space velocities to utilize CO as a reducing agent. For example, over the material EC-105, 5.3% conversion of 1000 ppm NO in 16 percent O_2 was obtained at 1000°C . Incorporation of 1000ppm CO into the gas stream resulted in overall conversion of 34%. Activity of the catalyst was improved by supporting it on yttria-stabilized zirconia (YSZ). Under the same reagentless conditions described for EC-105, YSZ-supported EC-105 gave 11 percent NO decomposition. Including CO in the gas stream again increased conversion. The data presented in Figure 4 show this effect under an even more

Table 2.
Data for the Oxidation of 600ppm CO in 16% O_2 Over the Catalyst 6.3% EC-105/ Al_2O_3 . $1.8 \times 10^6 \text{ h}^{-1}$.

Temperature ($^{\circ}\text{C}$)	CO Conversion (%)
400	13
450	90
500	100

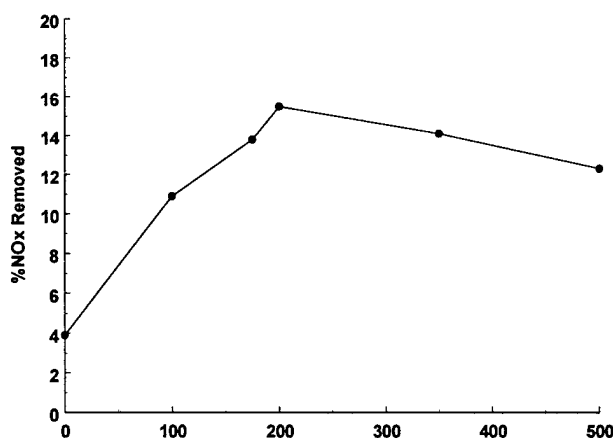


Figure 4. Plot of nitrogen oxides decomposed over 0.025 g of 4.3 wt% EC-105/YSZ. 477ppm NO, 16% O_2 . $T = 1000^{\circ}\text{C}$. GHSV = $800,000 \text{ h}^{-1}$. Overall flow rate = 365ml/min.

severe regimen: the conditions employed were 1000°C and 800,000h⁻¹ and 477 ppm NO. Using this supported catalyst 4 percent of the NO was removed absent CO and 16 percent when 200 ppm CO was included in the gas stream.

The results presented here show the capacity of these new catalysts to effect NO decomposition under conditions of high temperature and space velocity, conditions appropriate to near- and post-combustion environments.

CONCLUSIONS

New metal oxide catalysts possessing the brownmillerite structure have been synthesized and tested for direct NO_x decomposition activity. The catalysts have been shown to possess significant activities over a range of conditions. Activity demonstrated under these conditions point to potential use in post- and near-combustion environments. Anticipated potential applications are in exhausts of gas turbines, high-temperature process heaters, lean-burn engines, and diesel engines. In these applications, it is expected that the catalysts would be deposited directly onto the walls of combustion chambers or on downstream fixturing. Data obtained point to the possibility of catalyst use absent added reductant.

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